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Prompt and Delayed Dissociation of Energy-Rich Larger Molecules

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Coexistence of prompt and delayed decay modes of energized polyatomic molecules is discussed with reference to the special features of larger molecules which makes it amenable to experimental observation by a suitable choice of initial conditions. The molecular parameters identified by the RRKM theory of unimolecular (delayed) decay suffice to characterize the prompt process as well. The expected "kinetic stability" of large molecules is thus not necessarily the rule, and fast processes are possible, suggesting the possibility of experimental control.

Energizing polyatomic molecules above the threshold for bond breaking does not result in the immediate appearance of fragments. This is unlike the prompt dissociation of diatomic molecules. Following Lindemann, the delayed dissociation of polyatomics is assumed to be due to the time required for the bond-breaking energy to become localized.[1] It is thereby possible for the activation process to be completed well before any extensive bond breaking takes place. Unlike a diatomic, a polyatomic molecule can fall apart "on its own", i.e., in a unimolecular process. Our question here is whether larger polyatomic molecules are just larger, or are there any new features that follow from the increased size. In the conventional paradigm, the larger the molecule is, the more ways there are of partitioning the energy amongst its many modes. Hence, large molecules are sometimes said to enjoy a "kinetic stability" in that the fluctuation necessary to localize the energy where it is needed is rare so that bond breaking is slow. There is a wealth of experimental evidence that this is indeed the case. The question we discuss is whether this kinetic stability is *necessarily* the case, whether dissociation of large molecules with sufficient energy must be a slow process. The question is not idle because the delay in dissociation increases exponentially with the molecular size so that even small energy-rich peptides are predicted to have very considerable kinetic stability.[2]

We here discuss one possible mechanism whereby polyatomic molecules can promptly dissociate. The mechanism will apply also to an ordinary sized polyatomic molecule. What is special about larger molecules is that (i) the mechanism may be more readily realized experimentally and (ii) the necessary conditions for its validity are more readily satisfied for a larger system. The discussion builds upon the conventional paradigm to show that in larger molecules a prompt and delayed mechanism can coexist, that the rates of both the fast and the delayed decay can be characterized by the same molecular parameters one is familiar with, and that the relative importance of the two pathways is subject to experimental control.

Over the years, there have been repeated attempts to enhance the rate of dissociation of polyatomic molecules. These have

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included the by now classic experiments on chemical activation,[3] which seek to place the needed energy so that it is near to (or, alternatively, far from) the site of the chemical transformation, activation using infrared multiphoton pumping[4,5] or UV excitation,[6] attempts at blocking the intramolecular energy transfer,[7] site selective excitation,[8,9] and most recently, ultrashort visible or UV excitation.[9−12] An important source of evidence for prompt dissociation is from the mass spectrometry of molecules of biological importance. A molecular ion is given as much as a microsecond or so in order to dissociate before its fragments are detected. However, because the molecules are large, they should be stable for longer (or even much longer). Yet a fragmentation pattern of peptide ions is observed. Mass spectrometry does not have a time resolution, so one cannot say if the dissociation is prompt. But one can say[2] that small peptide ions dissociate faster than they should if the energy is equipartitioned over the large molecule.

In the RRKM theory,[1] the molecule dissociates when energy in excess of a threshold E_o is localized in the "transition-state" configuration. States that satisfy this criterion are taken to dissociate within about a vibrational period. In other words, such states dissociate promptly. At the same total energy there are many more other states where not enough energy is localized in the transition-state configuration. The RRKM theory assumes that during and following activation, energy is first equipartitioned amongst all modes. The number of states $N_‡$ of the transition state is far smaller than the total number, N, of states in the energy range of interest, and the ratio $N_‡/N$ decreases (exponentially) with the size of the molecule. Depending on the structure of the transition state, the number $N_‡$ is either nearly constant or by itself increases with size. The reason the ratio $N_‡/N$ decreases is that N increases with size faster than $N_‡$ does. (A simple estimate is that $N_‡$ scales as $((E - E_o)/h\bar{\nu})^{s-1}/(s - 1)!$ while N scales as $(E/h\bar{\nu})^{s-1}/(s - 1)!$, where s is the number of vibrational modes and the mean frequency is $\bar{\nu}$.)

For a larger molecule, the number, $N_‡$, of states of the transition state is no longer small. On the other hand, the ratio $N_‡/N$ is smaller and will remain small even for energies well in excess of the threshold energy for bond breaking. These are the two parameters that are needed in the discussion below. We argue that, when $N_‡/N \ll 1$, the unimolecular decay will exhibit both a (weakly size dependent, cf., Figure 1) prompt and a much delayed component. The delay scales as $N_‡/N$. When $N_‡ \gg 1$, that is for large molecules with an excess energy, it is realistic to experimentally control the relative importance of the two components up to a point where the decay is primarily prompt, even though $N_‡/N \ll 1$. For a smaller molecule, the ratio $N_‡/N$ increases rapidly with increasing excitation energy until it is no longer small compared to unity. The ratio is small primarily when $N_‡$ is itself small, i.e., in the immediate post-threshold regime.

The mechanism that allows for the coexistence of a prompt and a delayed decay can be discussed in purely quantum mechanical terms.[13−15] The theory is based on using an effective Hamiltonian, H, to describe the bound states of the molecule.[16−18] Because the molecule can dissociate, H is not Hermitian and has an anti-Hermitian part, Γ, which describes the coupling to the continuum, $H = H - i\Gamma$. The decay rate is non-negative, and so Γ is a positive operator. The eigenvalues of Γ are not necessarily all of comparable magnitude. Quite to the contrary, when $N_‡/N$ is small, the eigenvalues will separate into two distinct classes. The large eigenvalues, $N_‡$ in number, correspond to the prompt decay. This separation occurs because the rank of Γ is $N_‡$, and as is discussed above, $N_‡$ is much smaller than the rank, N, of the Hermitian Hamiltonian, H. To see this separation in a simple limit consider the special case when H is fully degenerate, $\mathbf{H} = E\mathbf{I}$, where $\mathbf{I}$ is the identity matrix. Then the transformation that diagonalizes Γ will also diagonalize H. Since the rank of Γ is $N_‡$, it has only $N_‡$ finite eigenvalues, all the others being zero. This limit exhibits only prompt decay.[13] In the general case, one can still diagonalize $\mathbf{H}$ and Γ simultaneously,[14] and in that case, the other $N - N_‡$ eigenvalues are not zero but are much smaller than the $N_‡$ large rates. The average value of the eigenvalues in the two groups is plotted in Figure 1, and we reiterate that the large eigenvalues (prompt rates) hardly vary with the size of the molecule. Therefore, the quantumtheory shows that, when $N_‡/N$ is small, there will be a separation of time scales manifested as two epochs in the time evolution, giving rise to prompt and delayed components in the appearance of products. In the following discussion, we shall use the language of the RRKM theory. This brings about the simplification that there are but two decay rates, a prompt and a delayed one (Figure 1) leading to a biexponential time evolution. The weights of the two exponents depend on the details of the initial excitation.

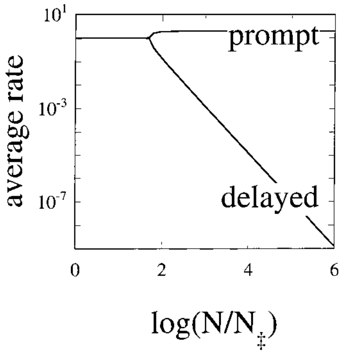

Figure 1. Decay rate (logarithmic scale) of an energy-rich polyatomic molecule versus the ratio of the number N of states of the molecule in the energy interval of interest and the number $N_‡$ of states of the transition state, $N_‡ \leq N$. In the $N_‡$ states, which are the gateways to the products, the energy is already localized where it is needed for dissociation. The Lindemann mechanism assumes that $N_‡ \ll N$, and in this regime, the quantum mechanical results exhibit a bifurcation where there is both a prompt and a delayed decay. RRKM is a quantitative statement that the delayed rate is $k(N_‡/N)$, where k is the rate of dissociation from the transition state. The plot is obtained by computing the average rate for a quantum mechanical Hamiltonian. Note how, at low values of $N_‡/N$, the average slow rate scales as expected from the RRKM theory. The point is that, when there are only a few windows for dissociation, there is also a second, prompt decay component, whose decay rate is almost independent of the size of the molecule. The contribution of this prompt component to the time evolution is determined by the initial excitation; see Figure 2.

The condition $N_‡ \ll N$, which is well satisfied for large molecules, insures (cf. Figure 1) a delayed dissociation. The origin of the delay is that reaching the transition-state configuration acts as a bottleneck. The fraction of systems in the transition state, $N_‡/N$, is small so that, while the decay of the molecules at the transition state is prompt, the decay of other molecules is delayed. However, the very same condition also insures that there can be a prompt dissociation (Figure 1). This is the dissociation of the $N_‡$ systems in the transition state. The importance of this prompt component is determined by the occupancy of the transition state. For the purpose of this discussion, we note that the quantum mechanical time evolution can be mimicked by a simple kinetic model, as follows. All energy-rich states are grouped into two exclusive groups. Those that promptly decay are in the transition state, labeled TS, while the other states are kinetically stable.

$$[\mathrm{N}] \underset{k\downarrow}{\overset{k\uparrow}{\rightleftarrows}} [\mathrm{TS}] \xrightarrow{k} [\text{products}] \qquad (1)$$

where the square brackets denote concentrations. k is the rate constant for prompt dissociation, which determines the rate of appearance of products in terms of the number of molecules in the transition state d[products]/dt $= k[\mathrm{TS}]$. This rate equals the rate for decay of bound molecules, $-\mathrm{d}([\mathrm{N}]+[\mathrm{TS}])/\mathrm{d}t = k[\mathrm{TS}]$.

The RRKM approach assumes that prior to dissociation there is time for the population of bound molecules to equilibrate between the two groups (i.e., there is a representative sampling of the bound part of phase space). The ratio of the concentrations is then equal to the ratio of volumes in phase space $[\mathrm{TS}]/[\mathrm{N}] = k\uparrow/k\downarrow$ and $\mathrm{d}[\text{products}]/\mathrm{d}t = (kk\uparrow/k\downarrow)[\mathrm{N}] = k(k\uparrow/(k\uparrow + k\downarrow))([\mathrm{N}] + [\mathrm{TS}])$. The rate constant for the decay is thus slowed down by $k\uparrow/(k\uparrow + k\downarrow)$ because of the equipartioning of the energy prior to dissociation. One expects this reduction to be considerable because in general there are many more states in N than in TS; $N_\ddagger/N \ll 1$ so that $k\uparrow/k\downarrow \ll 1$.

Initial conditions are under the control of the experimentalist. So rather than making an equilibrium approximation, $[\mathrm{TS}]/[\mathrm{N}] = k\uparrow/k\downarrow \ll 1$, one can exactly solve the kinetic scheme (1). To do so, one must specify the initial ratio[19] of the concentrations of the molecules in the two groups, and this specification replaces the assumption of equilibrium made above. Then, the two equations that govern the time evolution of the population in N and TS are respectively

$$[\mathrm{N}](t) = ([N]_0/2)\exp[-(k + k\downarrow + k\uparrow)t/2]\left[\left(1 - \frac{k + k\downarrow - k\uparrow}{\kappa}\right)\exp(-\kappa t/2) + \left(1 + \frac{k + k\downarrow - k\uparrow}{\kappa}\right)\exp(\kappa t/2)\right] + [TS]_0\frac{k\downarrow}{\kappa}\exp[-(k + k\downarrow + k\uparrow)t/2][\exp(\kappa t/2) - \exp(-\kappa t/2)] \qquad (2)$$

$$[TS](t) = [N]_0\frac{k\uparrow}{\kappa}\exp[-(k + k\downarrow + k\uparrow)t/2][\exp(\kappa t/2) - \exp(-\kappa t/2)] + ([TS]_0/2)\exp[-(k + k\downarrow + k\uparrow)t/2]\left[\left(1 + \frac{k + k\downarrow - k\uparrow}{\kappa}\right)\exp(-\kappa t/2) + \left(1 - \frac{k + k\downarrow - k\uparrow}{\kappa}\right)\exp(\kappa t/2)\right] \qquad (3)$$

where $\kappa^2 \equiv (k + k\uparrow + k\downarrow)^2 - 4k\uparrow k$. The kinetic model shows that attempting to vary the initial conditions is worthwhile. If initially all (or most) of the molecules are in N, i.e., have their energy nearly equipartitioned, then the exact time evolution is essentially that given by RRKM, namely the dissociation is delayed (lower panel of Figure 2).[20] When one puts $[\mathrm{TS}]/[\mathrm{N}] \ll 1$ as the initial condition, then the exact solution preserves this near equipartition and, as seen in the bottom panel of Figure 2, the concentration of molecules in the TS remains very low. The reason is that if a molecule makes it to the transition-state configuration, it promptly dissociates. So molecules do not accumulate there.

For larger molecules, one can depart from the RRKM initial conditions and thereby control the time evolution. If initially most molecules are created with the energy localized in the transition-state configuration, then the dissociation can be quite prompt (top panel of Figure 2). In other words, an activation where initially $[\mathrm{TS}]/[\mathrm{N}] \gg 1$ will lead to a dominant promptly dissociating component.

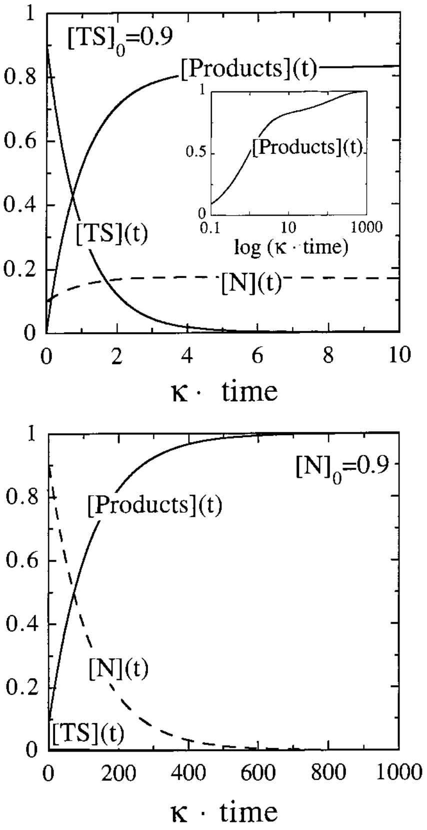

Figure 2. Prompt and delayed time evolution of the concentration (square brackets) of energy-rich molecules and of the products for the same system for two different initial conditions. Note the 2 orders of magnitude difference in the time scale. κ is a rate defined in ref 20 so that $\kappa \times$ time is dimensionless. The two equations that govern the time evolution in the TS and N are given by eqs 2 and 3. Top panel: initial excitation primarily in the transition state (TS) region. The decay of the molecule and the rise of the products are prompt. There is a small component of delayed decay (10% due to the initial excitation and a few additional percents due to the internal energy relaxation). This is reflected (see inset) in the rise of the concentration of the products at very long times (logarithmic scale). Bottom panel: initial excitation primarily of states where the excess energy is delocalized. The decay is far slower and the concentration of molecules in the transition state is negligible.

How far can one beat RRKM by a suitable initial preparation? In the kinetic scheme, it depends on the ratio $k\downarrow/k$. Intuitively this is clear. The energy-rich molecule, with its energy localized, has two choices: it can promptly dissociate or it can proceed to equipartition its localized energy. The branching ratio is $k\downarrow/k$. The larger it is, the more molecules will proceed towards energy redistribution. Since the rate constant k of prompt dissociation is quite large, as high as a vibrational frequency, the ratio $k\downarrow/k$ cannot be very large since it has the physical interpretation as the probability of energy redistribution per vibrational period. Ordinarily, this probability is well below unity, as otherwise a state of the transition state will dissipate its energy localization before it undergoes the motion along the reaction coordinate that will take it towards products.[21,22]

Molecular dynamics simulations (e.g., ref 23) suggest that molecules with enough energy for dissociation do retain their energy localization for tens (or more) of vibrational periods. Experimental evidence comes, for example, from attempts to quench the energy-rich molecules by collisions with other molecules. So far, there is no unequivocal evidence for the so-called Kramers "inverted regime",[24] where the frequency of collisions is so high that they can intercept a molecule during its motion along the reaction coordinate enroute from reactants to products. Figure 2 is drawn for the case $k{\downarrow}/k = 0.1$, which on the basis of the available evidence (see, for example, ref 25) is, if anything, an overestimate. For this value, only 10% of the molecules that are created in the transition state sample other configurations before dissociation. Therefore, prompt decay is the dominant decay mode, even when not all the molecules that are initially excited have their energy localized.

The conclusions of the simple kinetic model are fully supported by the quantum mechanical computations. Why then are there but few experimental reports of prompt decay of energy-rich molecules? One reason is that it is necessary to have the experimental time resolution. Only in large molecules is the slow decay so slow that a decay which occurs on the submicrosecond time scale must be due to a prompt process. In ordinary energy-rich polyatomics, the slow decay is itself quite fast and it needs a pump–probe time-resolved experiment to detect a prompt component. The second reason is that the presence of the prompt decay is only important if the initial excitation creates a sufficient number of molecules with the energy localized. Otherwise, the decay will be delayed.

A separation in time scales in the decay, leading to a distinguishable prompt and delayed components requires (cf. Figure 1) that $N_{\ddagger}/N \ll 1$ or $k{\uparrow}/k{\downarrow} \ll 1$. This condition is that most states of the energy-rich molecule do not have the energy localized. Collisional or chemical activation tends to produce only moderate deviations from uniformity of all quantum states.[26] Hence, such processes will usually not preferentially populate states of the transition state. Larger molecules are better candidates because $N_{\ddagger}$ is not small, and so the transition state is easier to access. This will be particularly so for selective excitation, e.g., by optical means, which due to Franck–Condon considerations, places the initially created energy-rich molecule in a very restricted configuration. The need then is to find such molecules where the Franck–Condon region is at or near the transition state.[27] Photodetachment experiments[28] and the NeNuPo pump–probe scheme[29] provide another route to this goal and are possible to implement also for larger molecules.

Diau et al.[11] report ultrafast activation of cyclic ketones, which eliminate CO by a Norrish type I two-step mechanism where a C–C bond is broken first. The energy-rich radical $CH_2-(CH_2)_n-C{=}O$, $n = 2, 3, 4$, and 10, then dissociates to form CO. This process is monitored by an ultrafast probe that ionizes the species, and the mass spectrum is recorded. Therefore, the time profile of both the decay of the parent and the rise of the products is determined. Earlier experiments by Kim et al.[10] suggested that for the second step in the dissociation of ketones the excitation is localized in the $CH_2-C{=}O$ region of the molecule, albeit possibly nonuniformly. Since the rate measured by Kim et al. is comparable for the acetyl and propionyl radicals, we shall take it as the prompt rate of dissociation of the $CH_2-C{=}O$ moiety. For the larger radicals, $n > 0$, Diau et al. report rates of decay of the parent or of the formation of products that are comparable to those of $n = 0$. This is consistent with the kinetic model discussed above if the initial energy deposition is largely localized in the $CH_2-C{=}O$ region irrespective of the size of the radical. Since the prompt lifetime is of the order of 100–200 fs, it is at most 10-fold slower than a vibrational C–C stretch frequency so that the fraction of molecules that promptly decay should be considerable.

It is reiterated that the fast activation is a necessary but not sufficient condition for the prompt decay. It is equally necessary that the initial activation accesses configurations where the energy is localized. Otherwise, the decay will be delayed even when the excitation is fast. In the experiments of Diau et al. the C=O group is the chromophore and so is the site of the excitation. The larger changes in bond lengths between the ground and electronically excited state occur therefore in the C–C=O moiety. Upon excitation, the Franck–Condon region is where these atoms are displaced from their equilibrium positions, and so it is this region of the molecule that is energy rich. That this region is also the gateway to the continuum is what makes the prompt decay observable. The success of Diau et al. is not only that they beat the time scale for energy redistribution. It is as much that they achieved a selective excitation that placed the energy-rich molecule at or near the transition state.

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(19) The ratio is all that is needed because the sum does not really matter. The kinetic equations are linear so that if one doubles the amount of starting material the solution is unchanged except that all concentrations double.

(20) There is one caveat. To have a quantitative agreement with the RRKM time evolution it is necessary that $\kappa^2 \equiv (k + k{\uparrow} + k{\downarrow})^2 - 4k{\uparrow}\, k > 0$, which means, in agreement with the spirit of RRKM, that the rate $k{\uparrow}$ is small.

(21) The observation[22] of discrete steps in the delayed decay, as a function of energy, steps which occur when $N_{\ddagger}$ increases by unity, shows that the energy of the states of the transition state is fairly well defined and hence that the rate of their dissipation is low.

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